

REMARKS

In view of the above amendments and the following remarks, reconsideration and further examination are requested.

The Examiner has made a number of objections to the specification. The specification and abstract have been reviewed and revised to make a number of editorial revisions and to address the Examiner's objections. Due to the number of changes involved, a substitute specification and abstract have been prepared and are submitted herewith. No new matter has been added. Enclosed is a marked-up copy of the specification and abstract indicating the changes incorporated therein. As a result, withdrawal of the objections is respectfully requested.

The Examiner has objected to Figures 1 and 13 for having improper reference signs 11 and 13, respectively. Substitute formal drawings are submitted herewith including amendments to Figures 1, 13, 16A and 16B. Figure 1 has been amended to remove reference sign 11 therefrom. Figure 13 has been amended so as to change reference sign 13 to W. Figures 16A and 16B have been amended so as to label the arrow in each of the figures with the reference sign A. No new matter has been added by these amendments. As a result, withdrawal of the objection to the drawings is respectfully requested.

Claims 9 and 12 have been objected to as containing a number of informalities. Claims 3-9 and 11-23 have been rejected under 35 U.S.C. §112, second paragraph, as being indefinite. Claims 1-23 have been canceled without prejudice or disclaimer to the subject matter contained therein. New claims 24-35 have been added. As a result, the objection and rejection under 35 U.S.C. §112, second paragraph are no longer applicable.

Claim 1 has been rejected under 35 U.S.C. §102(e) as being anticipated by Uzoh (US 6,140,234). Claim 1 has been rejected under 35 U.S.C. §102(e) as being anticipated by Adams (US 6,143,155). Claims 1, 2 and 12 have been rejected under 35 U.S.C. §102(e) as being anticipated by Woodruff (US 6,309,524). Claim 10 have been rejected under 35 U.S.C. §102(b) as being anticipated by JP 63-26400. Claims 3 and 4 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Uzoh ('234) in view of Kishi (US 5,437,777). Claim 5 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Uzoh ('234) in view of Kishi and further in view of Reynolds (US 5,932,077). Claim 6 has been rejected under 35 U.S.C. §103(a) as being unpatentable

over Uzoh ('234) in view of Kishi and further in view of JP 3-146698. Claim 7 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Uzoh ('234) in view of Kishi and JP 3-146698 and further in view of Courduvelis (US 4,956,097). Claims 8 and 9 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Uzoh ('234) in view of Uzoh (US 6,117,784) and either Dahms (US 5,849,171) or Dahms (US 5,433,840). Claim 11 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Uzoh ('234) in view of Miyazawa (US 4,303,443). Claim 13 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff. Claims 14 and 15 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of Reynolds. Claims 16 and 17 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of JP 3-146698. Claim 18 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of Reynolds and further in view of JP 3-146698. Claim 19 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of JP 3-146698 and further in view of Courduvelis. Claims 20 and 21 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of Uzoh ('784) and either Dahms ('171) or Dahms ('840). Claim 22 has been rejected under 35 U.S.C. §103(a) as being unpatentable over Woodruff in view of Miyazawa. Claim 23 has been rejected under 35 U.S.C. §103(a) as being unpatentable over JP 63-26400 in view of Nobel (US 3,833,486).

As discussed above, claims 1-23 have been canceled and are replaced with new claims 24-35. It is noted that claim 24 is similar to original claim 2.

With regard to Woodruff, it is not prior art that can be used against at least the electroless plating aspects of the current claims of the present invention for the following reasons. Woodruff is a continuation of international application PCT/US99/15847 filed on July 12, 1999, which is a continuation of: (1) U.S. application number 09/113,723 filed on July 10, 1998, now U.S. patent number 6,080,291; (2) provisional U.S. application number 60/111,232 filed on December 7, 1998; and (3) provisional U.S. application number 60/119,668 filed on February 11, 1999.

The present application is a national phase application of international application number PCT/JP99/04349 filed on August 11, 1999. The present application claims priority to three Japanese applications: (1) JP 10-239490 filed on August 11, 1998; (2) HP 11-30230 filed February 8, 1999; (3) JP 11-220363 filed on August 3, 1999. It is submitted that new claims 24-35 are supported by

JP 10-239490 filed on August 11, 1998. Enclosed herewith is a English language translation of JP 10-239490 along with a statement verifying the accuracy of the translation as evidence of the asserted support. As a result, claims 24-35 are entitled to the foreign priority date of August 11, 1998.

In light of the fact that claims 24-35 are entitled to the priority date of August 11, 1998, it is apparent that of all of the applications from which Woodruff claims priority, only U.S. application number 09/113,723, now U.S. patent number 6,080,291, has an earlier filing date, July 10, 1998. However, after reviewing U.S. patent number 6,080,291, it appears that at least the subject matter associated with electroless plating relied upon in the above-mentioned rejections is not disclosed in U.S. patent number 6,080,291. In fact, U.S. patent number 6,080,291 only discloses electroplating. Therefore, the subject matter in Woodruff associated with electroless plating is not entitled to the date of July 10, 1998. As a result, since all of the other relevant dates associated with Woodruff are after the August 11, 1998 priority date to which present claims 24-35 are entitled, Woodruff cannot be relied on as disclosing subject matter associated with electroless plating as recited in claims 24 and 29-35.

Further, the above-mentioned rejections are submitted to be inapplicable to the new claims for the following reasons.

Claim 24 is patentable over the references relied upon in the above-mentioned rejections, since claim 24 recites an apparatus having an electroless plating bath for forming an initial layer on a surface of a substrate by electroless plating; an electrolytic plating bath for filling a wiring recess with a metal by electrolytic plating, wherein the initial layer serves as a feeding layer for the electrolytic plating; and a transfer mechanism having an arm for transferring the substrate between the electroless plating bath and the electrolytic plating bath. None of the references, alone or in combination, disclose or suggest these features as recited in claim 24.

Uzoh ('234) discloses a method to selectively fill recesses with a conductive metal. The method includes depositing a seed layer 6 with either a CVD method or an electroless plating method on a barrier layer 4 of an insulating layer. After some additional operations, a conductive metal 8 is electroplated in recesses of the seed layer 6. (See column 3, lines 55-67 and column 4, lines 24-26).

While Uzoh ('234) discloses depositing the seed layer 6 with either CVD method or the electroless plating method and electroplating the conductive metal 8 of the seed layer 6, Uzoh ('234)

fails to disclose or suggest an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24. As a result, Uzoh ('234) fails to disclose or suggest the present invention as recited in claim 24.

Adams discloses a method for simultaneous non-contact electrochemical plating of semiconductor wafers using a bipolar electrode assembly. The method includes depositing a thin seed layer 80 on a barrier and adhesion layer 70 by CVD, PVD or electroless plating and then filling a trench with a metal fill 90 by CVD, PVD, electroless or electrolytic plating. The bipolar electrode assembly for electrolytic plating is disclosed with different embodiments. (See column 5, line 60 - column 6, line 5 and Figures 4 and 5).

While Adams discloses depositing the seed layer 80 with CVD, PVD or electroless plating, electroplating the metal fill 90 on the seed layer 80 by CVD, PVD, electroless or electrolytic plating, and the assembly for electrolytic plating, Adams fails to disclose or suggest an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24. As a result, Adams fails to disclose or suggest the present invention as recited in claim 24.

As for Woodruff, as discussed above, Woodruff cannot be relied upon as disclosing at least an electroless plating bath as recited in claim 24. As a result, Woodruff fails to disclose or suggest the present invention as recited in claim 24.

JP 63-26400 discloses a device that has a number of valves 21-23, 27 and 38 which can be selectively opened to allow a number of different solutions into a plating cell 1. (See Abstract and Figure 1). However, JP 63-26400 fails to disclose or suggest an apparatus having an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24. As a result, JP 63-26400 fails to disclose or suggest the present invention as recited in claim 24.

Kishi discloses an apparatus for forming a metal wiring pattern for a semiconductor device. The apparatus is disclosed as two separate embodiments. The first embodiment is an electroless plating apparatus (see column 3, lines 61-68) and the second embodiment is an electroplating apparatus (see column 5, lines 10-14). While Kishi discloses an electroless plating apparatus and an electroplating apparatus as separate embodiments, Kishi fails to disclose or suggest an apparatus having an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24. As a result, Kishi fails to disclose or suggest the present invention as recited in claim 24.

As for (1) Reynolds, (2) JP 3-146698, and (3) Courduvelis, these references are relied upon as disclosing (1) a megasonic transducer 70 (see column 4, lines 44-46), (2) a preparation vessel 25 (see abstract), and (3) waste treating a plating solution (see column 3, line 13 - column 4, line 5), respectively. However, none of these references discloses or suggests an apparatus having an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24.

Uzoh ('784) discloses a process for integrated circuit wiring. The process includes either electroplating or electroless plating a metal in opening in a photoresist pattern to form the wiring. (See column 3, line 37 - column 4, line 20). However, Uzoh ('784) fails to disclose or suggest an apparatus having an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24. As a result, Uzoh ('784) fails to disclose or suggest the present invention as recited in claim 24.

As for (1) Dahms ('840) and (2) Dahms ('171), these references are relied upon as disclosing (1) an acid bath for the galvanic deposition of copper, and (2) and an acid bath for copper plating, respectively. However, (1) Dahms ('840) and (2) Dahms ('171) fail to disclose or suggest an apparatus having an electroless plating bath, and electrolytic plating bath, and a transfer mechanism as recited in claim 24.

As for (1) Miyazawa and (2) Nobel, these references are relied upon as disclosing (1) a electroless copper plating solution and (2) a plating bath, respectively. However, Miyazawa and Nobel fail to disclose or suggest an apparatus having an electroless plating bath, an electrolytic plating bath, and a transfer mechanism as recited in claim 24.

Since none of the above-discussed references discloses or suggests the present invention as recited in claim 24, it is submitted that no combination of the references discloses or suggests the invention because all of the references are lacking the same features of claim 24.

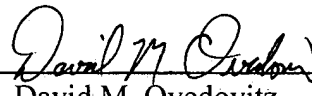
Claim 2 has been rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claim 1-72 of Hongo (US 6,294,059). In light of this rejection, a Terminal Disclaimer linking the present application with Hongo is submitted herewith. As a result, withdrawal of this rejection is respectfully requested.

Because of the above mentioned distinctions, it is believed clear that claims 24-35 are allowable over the references relied upon in the rejections. Furthermore, it is submitted that the distinctions are such that a person having ordinary skill in the art at the time of invention would not have been motivated to make any combination of the references of record in such a manner as to result in, or otherwise render obvious, the present invention as recited in claims 24-35. Therefore, it is submitted that claims 24-35 are clearly allowable over the prior art of record.

In view of the above amendments and remarks, it is submitted that the present application is now in condition for allowance. The Examiner is invited to contact the undersigned by telephone if it is felt that there are issues remaining which must be resolved before allowance of the application.

Respectfully submitted,

Akihisa HONGO et al.

By: 
David M. Ovedovitz
Registration No. 45,336
Attorney for Applicants

DMO/jmj
Washington, D.C. 20006-1021
Telephone (202) 721-8200
Facsimile (202) 721-8250
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DESCRIPTION

SUBSTRATE PLATING METHOD AND APPARATUS

Technical Field

5 **[0001]** The present invention relates to a method and apparatus for plating a substrate, and more particularly to a method and apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with wiring metal such as copper, copper alloy, or the like.

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Background Art

15 **[0002]** Conventionally, in order to form a wiring circuit on a semiconductor substrate, a layer of Al or Al alloy is deposited on a surface of a substrate by a sputtering process or the like, and then unnecessary portions are removed from the layer by a chemical dry etching process using a photoresist or the like for a mask pattern. However, as the level of integration of circuits increases, the width of wiring becomes narrower to thus increase current density, resulting in generating thermal stress in the wiring and increasing temperature of the wiring. As a result, the layer of Al or Al alloy becomes thinner due to stress migration or electromigration, and finally to cause a breaking of the wiring.

25 **[0003]** Hence, copper has been drawn much attention as a wiring material because of its lower resistance and higher reliability. However, it is difficult to form wiring by etching after a layer is deposited on a surface of a

substrate and then performing a patterning process—is
performed, which is differently different from a
conventional method using Al. Therefore, there has been
attempted a damascene process in which a wiring groove is
5 preformed in a substrate and filled with copper by chemical
vapor deposition (CVD), sputtering, plating, or the like,
and then unnecessary portions are removed from the surface
of the substrate by chemical mechanical polishing (CMP), for
thereby forming wiring in the groove.

10 [0004] Among these processes for filling a wiring groove
with copper, the plating process has drawn much attention
because of the following advantages. The processing cost is
lower than that in other processes, and pure copper material
can be obtained, and the process can be performed at such a
15 low temperature that a substrate is not damaged. The
plating process mainly comprises an electroless plating
process, which is mainly performed by a chemical process,
and an electrolytic plating process, which is performed by
an electrochemical process. The electrolytic plating
20 process is generally more efficient than the electroless
plating process.

[0005] Since copper is liable to be oxidized and
corroded and diffused into SiO_2 , wiring is generally formed
after a wiring portion on a base material of the substrate
25 is covered with a barrier layer of metal nitride such as
TiN, TaN, and WN. Since the sheet resistance of this
barrier layer is prohibitively larger than the resistance of
the plating liquid, it has been difficult to perform uniform

electrolytic plating on the barrier layer formed over the surface of the substrate.

5 [0006] Conventionally, a seed layer of copper is formed on the barrier layer by a sputtering process or a CVD process, and then plated with copper by an electrolytic plating process to fill fine recesses formed in the substrate with copper. However, it is difficult to uniformly deposit a layer on a wall of the fine recess by the sputtering process, and the CVD process introduces
10 impurities into the deposited layer. Further, when the design rule is further decreased from about 0.18 μm to 0.10 μm , there is no dimensional margin to form a seed layer having a thickness of 0.02 to 0.05 μm within the recess.

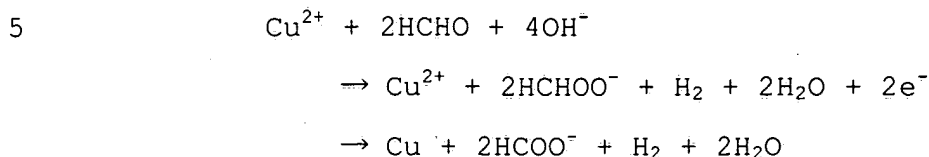
15 [0007] On the other hand, in the electroless plating process, since the plating layer is grown in isogonic directions from a side wall or a bottom surface of the fine recess, an inlet of the recess is covered with metal grown from the side wall and hence, a void tends to be formed in the recess. In addition, since the plating rate of the
20 electroless plating process is about one-tenth as slow as that of the electrolytic plating process, the electroplating process is inefficient.

Summary Disclosure of the Invention

25 [0008] It is therefore an object of the present invention to provide a method and apparatus for plating a substrate to form wiring by efficiently filling a fine recess formed in a semiconductor substrate with plating

metal without a void or contamination.

[0009] When formalin (HCHO) is used in the electroless plating process as a reducing agent, hydrogen gas (H₂) is generated according to the following reaction.



[0010] When a plating surface of a substrate W faces downwardly or sideways, as shown in FIGS. 16A and 16B, bubbles 98 are generated by hydrogen gas (H₂) in a plating liquid Q within recesses 42, such as fine grooves or the like, formed in the substrate, and these bubbles cause a plating defect 99. In order to prevent the generation of these plating defects 99, a pump or air is generally used to
15 agitate the plating liquid in the conventional plating process. However, as shown in FIG. 16B, unevenly plated portions 100 are generated on a plating surface 97 of the substrate W in the direction that the hydrogen gas bubbles 98 move, indicated by ~~the~~ an arrow A.

20 **[0011]** In order to remove the bubbles 98 from the plating surface 97, the conventional methods employ a jig to grip or suspend the plating substrate W, while a shock is applied externally to the jig to separate the bubbles from the plating surface 97. However, since there is risk that
25 the shock will damage the jig or the plating substrate, this method is not desirable.

[0012] A conventional electroless plating apparatus comprises a plating processing tank and a plating liquid

circulating tank, and a plating liquid is circulated during the plating process. The plating liquid is prepared in a special preparation bath or in the circulating tank. Therefore, problematic reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, occur in the electroless plating liquid immediately after preparation to cause deterioration of the plating liquid and changes in concentration of the plating liquid composition.

10 | [0013] Accordingly, it is another object of the present invention to provide a method and apparatus for electroless plating which can minimize the amount of plating defects and unevenly plated portions and can prevent deterioration of a plating liquid and changes in concentration of the plating liquid composition to perform a plating process with a highly stable quality.

| [0014] In the conventional electrolytic plating, in order to grow a uniform layer in through holes formed in a printed circuit board using copper plating, the concentration of copper in the plating liquid is lowered to improve the throwing power (in a high throwing power bath). This is because the overvoltage of a cathode is increased by increasing the polarization of the cathode to improve the throwing power. A degree of liquid flow through the holes can be expected when the dimensions of the holes in the printed circuit board are about 50 to 100 μm .

25 | [0015] The wiring grooves or holes formed in a surface of a semiconductor wafer have a width or diameter of 0.2 μm

or less and do not pass through the substrate. Hence, it is impossible to flow a liquid through such fine grooves or holes. Further, the electrophoresis speed generated by the electric field is numerically small, and hence the holes are filled with copper ions almost entirely by the diffusion of ion concentration. The amount of diffusion of copper ions in the holes decreases in proportion to the second power of the hole diameter (the area of the inlet of the hole) as the hole diameter decreases.

10 [0016] In contrast, the amount of deposition of copper ions in the hole grows smaller in proportion to the diameter of the hole. Accordingly, copper ions can be expected to be diffusion-controlled in grooves and holes, as semiconductor devices become more integrated and the width of grooves and diameters of holes become smaller in the future. When the hole diameters drop below $0.15 \mu\text{m}$, in particular, copper ions tend to be diffusion-controlled depending on a method of agitating plating liquid for a large aspect ratio.

20 [0017] Therefore, it is another object of the present invention to provide a method and apparatus of electrolytic plating capable of sufficiently filling a fine groove and a hole formed in a surface of a substrate using a copper plating without copper ions becoming diffusion-controlled in the groove and the hole, even when the width of the groove and the diameter of the hole become smaller and the integration in the semiconductor devices increases.

25 [0018] According to a first aspect of the present invention ~~defined in claim 1~~, there is provided a method of

plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, the method comprising: performing an electroless plating process of forming an initial layer on a substrate; and performing an electrolytic plating process of filling the wiring recess with plating metal while the initial layer serves as a feeding layer.

[0019] With this method, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, an electroless plating process with high uniformity is combined with an electrolytic plating process having good qualities in leveling and high-speed filling. The recess having a barrier layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. By filling the greatest portion of the recess formed on the feeding layer with the electrolytic plating, it is possible to maintain a high plating speed and increase throughput.

[0020] The electroless plating process and the electrolytic plating process may be performed in the same plating processing tank or in separate processing tanks. Further, the same plating liquid may be used in the same plating processing tank to perform both of the electroless plating process for forming an initial layer serving as a feeding layer and the electrolytic process for filling the

recess. With this method, both of the plating processes can continuously be performed without changing the processing tank or the plating liquid, for thereby simplifying the apparatus and process while achieving the above effects.

5 | [0021] According to a second aspect of the present invention ~~defined in claim 2~~, there is provided an apparatus for plating a substrate to fill a wiring recess in a semiconductor substrate with plating metal, the apparatus comprising: an electroless plating tank for forming an
10 | initial layer on a substrate by electroless plating; an electrolytic plating tank for filling the wiring recess with plating metal while the initial layer serves as a feeding layer; and transfer means for transferring a substrate between the tanks.

15 | [0022] With this apparatus, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, the recess having a barrier
20 | layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. The electroless plating tank and the electrolytic plating tank should preferably be disposed in close proximity to
25 | each other within the same space and separated by a partition.

| [0023] By providing a substrate transfer means in addition to the electroless tank and the electrolytic

plating tank, it is possible to continue from one process to the next process without changing the state of the surface of the substrate when transferring the substrate. Specifically, the electroless plating tank, the electrolytic plating tank, and required rinse tanks should preferably be arranged in close proximity to each other, and the substrate should be transferred after the plating process or the rinsing process, without exposing the surface of the substrate to the air. Such a function may also be provided in the transfer means itself.

[0024] According to a third aspect of the present invention defined in claim 3, there is provided a method or apparatus for plating a substrate according to the first or second aspect claim 1 or 2, comprising in the electroless plating process or the electroless plating bath: means for disposing a substrate to be plated in such a state that a surface to be processed thereof faces upwardly, and forming a hermetically sealed space by the surface to be processed; and plating liquid supply means for supplying an electroless plating liquid to the hermetically sealed space to perform an electroless plating process.

[0025] By facing the plating surface of the substrate to be plated upwardly, nitrogen gas bubbles certainly generated in the plating liquid in the electroless plating process will moved upwardly due to buoyancy. Accordingly, the number and the amount of bubbles remaining on the plating surface of the plating substrate and in the fine groove and hole can be reduced, ~~for~~ thereby reducing the plating

defects.

[0026] According to a fourth aspect of the present invention defined in claim 4, there is provided a method or apparatus for plating a substrate according to the third aspect claim 3, wherein the minimum amount of electroless plating liquid required for performing a predetermined plating on the substrate to be plated is supplied to the hermetically sealed space, and the electroless plating process is performed with the electroless plating liquid in a static state. Since this method does not move the nitrogen gas bubbles over the plating surface, it is possible to minimize the unevenly plated portions that are generated on the plating surface, as shown in FIG. 17.

[0027] According to a fifth aspect of the present invention defined in claim 5, there is provided a method or apparatus for plating a substrate according to the third or fourth aspects claim 3 or 4, further comprising: pressure pulsation means for generating a pressure in the hermetically sealed space that is higher than atmospheric pressure and for pulsating the pressure.

[0028] According to the present invention, since the hydrogen gas bubbles can be encouraged to dissolve into the electroless plating liquid by pressurization, it is possible to encourage the nitrogen gas bubbles to separate from the plating surface. Specifically, the nitrogen gas bubbles 98 attached to the plating surface 97 of the plating substrate W, as shown in FIG. 11A, are contracted by pressurization, as shown in FIG. 11B, to separate from the plating surface

97. The nitrogen gas bubbles 98 are expanded by decompression, as shown in FIG. 11C, to separate completely from the plating surface 97.

5 [0029] According to a sixth aspect of the present invention ~~defined in claim 6~~, there is provided a method or apparatus for plating a substrate according to any one of the third ~~claims~~ 3 through 5 fifth aspects, further comprising a preparation bath disposed in the vicinity of the hermetically sealed space for supplying the minimum
10 amount of prepared electroless plating liquid to the hermetically sealed space just prior to the electroless plating process.

[0030] According to the present invention, the plating process is completed before an occurrence of problematic
15 reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, which cause deterioration of the plating liquid and changes in concentration of the plating liquid composition immediately after the preparation. Therefore, the plating process can
20 be performed with a highly stable quality.

[0031] According to a seventh aspect of the present invention ~~defined in claim 7~~, there is provided a method or apparatus for plating a substrate according to the sixth aspect ~~claim 6~~, wherein the electroless plating liquid is
25 processed as a waste liquid without circulating the electroless plating liquid after performing the electroless plating process with the minimum amount of electroless plating liquid.

[0032] According to the present invention, since the amount of plating liquid used per deposition (deposition of plating layer) can be maintained to be the minimum required amount, it is possible to avoid increases in cost with the waste liquid and an excessive burden on the environment.

[0033] The plating substrate may be held on a turntable in the electroless plating tank to be rinsed and dried after the plating process. With this arrangement, the plating, rinsing, and drying processes can all be performed in the same area, thereby reducing the space required for device installation and making the device suitable for installation in a clean room.

[0034] A hot bath for maintaining temperature may be provided in the electroless plating tank in the vicinity of the top of the hermetically sealed space, and a heater for maintaining temperature may be disposed below the plating substrate. With this arrangement, it is possible to maintain a fixed plating temperature, which is one of the most important factors governing the quality (uniformity of layer thickness, reproducibility, electric conductivity of the plating layer, etc.) of electroless plating.

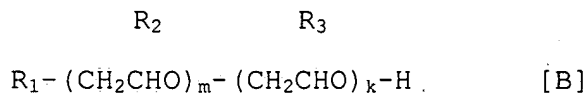
[0035] In the electroless plating process, the minimum required amount of electroless plating liquid may be set within a range of amount of liquid that includes ions of solutes 1.5 to 20 times as many as a predetermined deposited metal equivalent. In the electroless plating process, the pressure pulsation means may be configured to generate pressure pulsations having an amplitude of 0 to 1 MPa and a

frequency of 0 to 10 Hz.

[0036] According to an eighth aspect of the present invention ~~defined in claim 8~~, there is provided a method or apparatus for plating a substrate according to the first or second aspects claim 1 or 2, wherein the plating liquid used in the electroless plating process or the electroless plating bath comprises copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) having a concentration of 100 to 250 g/l, sulfuric acid (H_2SO_4) having a concentration of 10 to 100 g/l, and chlorine ions having a concentration of 0 to 100 mg/l.

[0037] According to a ninth aspect of the present invention ~~defined in claim 9~~, there is provided a method or apparatus for plating a substrate according to the eighth aspect claim 8, wherein the electrolytic plating liquid further comprises at least 0.14 to 70 $\mu\text{mol/l}$ of a sulfur compound expressed by a formula in [A] below, 10 to 5000 mg/l of a macromolecular compound expressed in a formula [B] below, and 0.01 to 100 mg/l of a nitrogen compound; wherein L is an alkyl group having a carbon number of 1 to 6 which is substituted by a lower alkyl group, a lower alkoxyl group, a hydroxyl group, or a halogen atom; and X is a hydrogen atom, a $-\text{SO}_3\text{M}$ group, or a $-\text{PO}_3\text{M}$ group (M indicating a hydrogen atom, an alkali metal atom, or an amino group) in the formula [A]; and ~~R1~~ R₁ indicates a residue of a higher alcohol group having a carbon number of 8 to 25, a residue of an alkyl phenol with an alkyl group having a carbon number of 1 to 25, a residue of an alkyl naphthol with an alkyl group having a carbon number of 1 to 25, a residue of

a fatty acid amide having a carbon number of 3 to 22, a residue of an alkylamine having a carbon number of 2 to 4, or a hydroxyl group; R_2 and R_3 indicate a hydrogen atom or a methyl group; and m and k indicate an integer from 1 to 100 in the formula [B].



[0038] Since increases in copper concentration in the plating liquid generate proportional increases in the diffusion speed, it is possible to prevent copper ions from becoming diffusion-controlled in the groove and the hole, even when the width of the groove and the diameter of the hole become smaller and the integration in the semiconductor devices increases. Of course, it is also possible to produce a thinner diffusion layer and suppress the current density by agitating the plating liquid.

[0039] FIG. 18 is a graph comparing diffusion amount and deposition amount in a hole H of $1.2 \mu m$ shown in FIG. 19. In FIG. 18, the vertical axis represents the amount of copper deposition and the amount of copper diffusion (g/s), and the horizontal axis represents the diameter ϕ (μm) of the hole H . Here, the diffusion coefficient is set at $0.72 \times 10^{-9} m^2/s$ and the diffusion layer thickness at $5 \mu m$. When the diffusion amount is greater than the deposition amount, the ions become reaction-controlled to prevent a depletion in copper ions in the hole H and the generation of voids therein. When the diffusion layer is less than the

deposition amount, the ions become diffusion-controlled, and voids are generated in the hole H. As seen in FIG. 18, higher concentrations of copper sulfate are advantageous when the hole diameter becomes finer, while the sulfuric acid concentration relatively declines due to the relationship with saturated concentration. By reducing the sulfuric acid concentration, the electrical resistance of the plating liquid increases, improving the uniformity of the deposited layer thickness.

10 | **[0040]** In FIG. 18, a curve A indicates the diffusion amount (per second) when the copper sulfate concentration is 225 g/l, a curve B indicates the deposition amount (per second) when the current density is 3 A/dm², a curve C indicates the deposition amount (per second) when the current density is 2.5 A/dm², a curve D indicates the deposition amount (per second) when the current density is 2 A/dm², and a curve E indicates the diffusion amount (per second) when the copper sulfate concentration is 75 g/l.

20 | **[0041]** As described above, the plating liquid includes the sulfur compound shown in equation [A] of 0.14 to 40 μ mol and the macromolecular compound shown in equation [B]. This sulfur compound can achieve a fine deposition. Some examples of these compounds include N, N-dimethyldithiocarbamylpropylsulfonic acid, O-ethyl-S-(3-propylsulfonic acid)-dithiocarbonate, bis-(sulfopropyl) disulfide, and their salts.

25 | **[0042]** In the present invention, the amount of additive in the sulfur compound should preferably be 0.14 to 70 μ

mol/l, since the amount of copper sulfate is greater than the amount of sulfuric acid. The amount of additive in the sulfur compound is less than that in the case where a solution with a low concentration of copper sulfate is used
5 because the cathode vicinity is rich in copper ions, requiring less sulfur compound as an accelerating agent.

[0043] Some examples of a macromolecular organic additive contained in the plating liquid are PPG and PEG, their random or block polymers, or a derivative thereof,
10 such as a polyether type. The amount of macromolecular organic additive is about 10 to 5000 mg/l.

[0044] A leveler is added to the above plating liquid to further control the copper deposition and accelerate plating growth in the bottom of the hole. The leveler is a nitrogen
15 compound containing a polyalkylene imine, such as a phenazine compound, a phthalocyanine compound, a polyethylene imine, and a polybenzyl ethylene imine, or a derivative thereof, or a thiourea derivative such as an N-dye substitute compound, a safranine compound, such as a
20 phenosafranine, a safranine azo naphthol, a diethyl safranine azo phenol, and a dimethyl safranine dimethyl aniline, or a polyepichlorohydrine or a derivative thereof, or a phenylthiazonium compound such as a thioflavine, or a amide type, such as an acrylamide, a propylamide, and a
25 polyacrylic acid amide. This nitrogen compound of about 0.01 to 100 mg/l is added as a leveler.

[0045] According to the present invention defined in a tenth aspect ~~claim 10~~, there is provided an apparatus for

plating a substrate to fill a wiring recess formed in a semiconductor substrate with plating metal, the apparatus comprising: one processing tank having an electroless plating liquid supply path for supplying an electroless plating liquid to form an initial layer on a substrate by an electroless plating process, and an electrolytic plating liquid supply path for supplying an electrolytic plating liquid to fill the wiring recess by electrolytic plating while the initial layer serves as a feeding layer; wherein the two paths are selectively switchable.

[0046] Hence, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. Since both of the electroless plating process for forming the initial layer and the electrolytic plating process for filling the recess can be performed continuously in the same processing tank, the equipment and time required to transfer the substrate can be minimized and the state of the surface of the substrate can be prevented from changing. A cleaning liquid supply path for cleaning a substrate may be disposed to perform a cleaning process in the same processing tank.

[0047] The processing tank may ~~hermetically~~ be hermetically sealed with a parallel flow. With this

arrangement, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus perform the efficient plating with sufficient flowability of the plating liquid.

5 **[0048]** According to an eleventh aspect of the present invention ~~defined in claim 11~~, there is provided a method or apparatus for plating a substrate according to any one of the first ~~claims 1~~ through tenth aspects 10, wherein the plating liquid used in the method or apparatus does not
10 include an alkali metal as a pH regulator.

Brief Description of Drawings

15 **[0049]** FIG. 1 is a plan view showing a whole structure of a plating apparatus according to a first embodiment of the present invention;

15 **[0050]** FIG. 2 is a side view showing a processing tank used in the plating apparatus of FIG. 1;

15 **[0051]** FIG. 3 is a cross-sectional view taken along a line A-A of the processing tank in FIG. 2;

20 **[0052]** FIG. 4 is a schematic view showing the processing tank used in the plating apparatus in FIG. 1 and circulating paths of a processing liquid;

15 **[0053]** FIG. 5 is a side view of the plating apparatus in FIG. 1;

25 **[0054]** FIG. 6 is a flowchart showing processes performed with the plating apparatus in FIG. 1;

15 **[0055]** FIGS. 7A through 7D are schematic diagrams explanatory of a process of plating a recess formed in a

substrate;

[0056] FIG. 8 is a schematic view showing a processing tank used in a plating apparatus according to a second embodiment of the present invention;

5 **[0057]** FIG. 9 is a plan view showing a whole structure of a plating apparatus according to a third embodiment of the present invention;

[0058] FIG. 10 is a schematic view showing a structure of an electroless plating device in FIG. 9;

10 **[0059]** FIGS. 11A through 11C are schematic diagrams explanatory of the behavior of hydrogen gas bubbles when pressure of a hermetically sealed space in the electroless plating device is pulsed;

[0060] FIG. 12 is a schematic view showing a structure of the electroless plating device in FIG. 9;

[0061] FIG. 13 is a schematic view showing a structure of an electrolytic plating device in FIG. 9;

[0062] FIG. 14 is an enlarged view of an area B indicated in FIG. 13;

20 **[0063]** FIG. 15 is a schematic view showing a processing tank used in the plating apparatus and circulating paths of a processing liquid according to the third embodiment of the present invention;

[0064] FIGS. 16A and 16B are schematic diagrams explanatory of the behavior of hydrogen gas bubbles in electroless plating, FIG. 16A shows the behavior of the hydrogen gas bubbles when a plating surface of a plating substrate faces downwardly, and FIG. 16B shows the behavior

of the hydrogen gas bubbles when the plating surface of the plating substrate faces sideways;

[0065] FIG. 17 is a schematic diagram explanatory of unevenly plated portions generated on a plating surface of a plating substrate by the behavior of hydrogen gas bubbles in electrolytic plating;

[0066] FIG. 18 is a graph comparing diffusion amount and deposition amount in holes formed in a plating substrate; and

[0067] FIG. 19 is a schematic view showing an example of a shape of a hole formed in a surface of a plating substrate.

Detailed Description of Best Mode for Carrying Out the Invention

[0068] Embodiments according to the present invention will be described below with reference to the accompanying drawings. A plating apparatus is disposed in a rectangular installation frame 10, as shown in FIG. 1. The plating apparatus has a clean zone 13 at one side of the installation frame 10, and load/unload units 14a, 14b and two cleaning and drying devices 60 for post-processing a substrate, after the plating process, are disposed at the clean zone 13. A transfer device (first transfer robot) 61 for transferring a substrate is provided among the load/unload units 14a, 14b and the cleaning and drying devices 60. The plating apparatus has a contaminated zone 12 at the other side of the installation frame 10, and a

second transfer robot 62 movable on a rail is disposed at the central portion of the contaminated zone 12. An SnCl_2 solution tank 16 containing SnCl_2 solution used as an activator in plating, a rinse tank 17, a PdCl_2 solution tank 18 containing PdCl_2 solution used as a catalyst in electroless plating, and a rinse tank 19 are disposed in order on one side with respect to the second transfer robot 62. An electroless plating tank 20, a rinse tank 21, an electrolytic plating tank 22, and a rinse tank 23 are disposed in order on the other side with respect to the second transfer robot 62. The rinse tanks 17, 19, 21 and 23 may be provided as needed.

[0069] Each of these processing tanks 16-23 has the same basic shape and structure, and comprises a processing container body 50 having a rectangular plate shape and a recess 50a forming a processing chamber 52 therein, and a cover 51 capable of opening and closing a front opening of the processing container body 50, as shown in FIG. 2. A packing 53 is mounted at the peripheral portion of the processing container body 50 to maintain the water-tightness of the processing container body 50 when the cover 51 is closed and brought into close contact with the processing container body 50. A holding member for detachably holding a substrate W is provided on the inner side of the cover 51, and the cover 51 is provided with a sensor (not shown) for detecting the existence of a substrate W on the holding member.

[0070] In the processing tank (electrolytic plating

tank) 22 for performing electrolytic plating, a plate-like anode 54 is mounted on the bottom of the recess 50a in the processing container body 50 in parallel with the processing chamber 52, and a shielding plate 55 made of dielectric material is disposed at the opening end of the recess 50a. The shielding plate 55 has an opening 55a therein for regulating the electric field on a plating surface of the substrate W. The other processing tanks are not provided with the anode 54 or the shielding plate 55.

10 [0071] An upper header 56 and a lower header 57 are mounted on the top and bottom of the processing container body 50 and ~~communicated~~ communicate with the processing chamber 52 via a plurality of through-holes 56a, 57a, respectively. Thus, for example, a processing liquid is supplied from the lower header 57 to the upper header 56 to thus generate a parallel flow along the surface of the substrate to be plated, as shown in FIG. 3. As shown in FIG. 4, processing liquid circulating devices 33 each having a reservoir tank 31 and a circulating pump 32 are provided below the processing tanks 16-23, and a supply pipe 34 and a return pipe 35 extending from the processing liquid circulating device 33 are connected to the lower header 57 and the upper header 56.

25 [0072] Since, as described above, the plating tanks 20, 22 are hermetically sealed with a parallel flow, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus perform the efficient plating with sufficient flowability of the plating liquid.

Further, each of the processing tanks 16-23 is vertically positioned, and hence bubbles in fine recesses formed in the substrate W can easily flow out therefrom during the plating process or the like. Therefore, uniformity of the plating
5 reaction and the processing rate can be increased, and simultaneously the installation area of the processing tanks 16-23 can be reduced, resulting in an efficient arrangement of the processing tanks.

[0073] In this embodiment, the transfer robot 62
10 comprises a hexaxial robot having a plurality of arms 63 and a hand 64 which is provided on the end of the arms 63 and is capable of opening and closing (see FIG. 5). A plurality of rollers 65 are rotatably supported on the inner surface of the hand 64. A temporary holding stage 66 having a
15 plurality of supports is provided in the clean zone 13 and used for temporarily holding a substrate W to be transferred between the clean zone 13 and the contaminated zone 12.

[0074] Next, the plating process according to the plating apparatus thus constructed will be described below
20 with reference to FIGS. 6 and 7. The first transfer robot 61 takes out a substrate W held on the load/unload unit 14a, 14b and places the substrate W on the temporary holding stage 66. The second transfer robot 62 transfers the substrate W to the contaminated zone 12, and, when
25 necessary, the substrate W is inserted into the processing container body 50 of the activation tank 16 and activated by a processing liquid containing an activator such as SnCl_2 . Next, the substrate W is transferred to the adjacent rinse

tank 17 to be rinsed, and then transferred to the catalyst application tank 18 to receive a catalyst application.

[0075] In this process, Sn^{2+} ions from the activator are adsorbed by the surface of the substrate W in the activation tank 16, and these ions are oxidized in the catalyst application tank 18 to be Sn^{4+} . On the other hand, Pd^{2+} ions are reduced to Pd metal, and the Pd metal is deposited on the surface of the substrate W to serve as a catalyst in the following electroless plating process. A single catalyst containing Pd/Sn colloids may be used in this process. In this embodiment, the catalyst application process described above is performed in the activation tank 16 and the catalyst application tank 18 belonging to a portion of the plating apparatus. However, the catalyst application process may be performed in a separate apparatus, and then the substrate W may be transferred to the plating apparatus. It is possible to dispense with the activation process and/or the catalyst application process in some cases, depending on a material or a state of the inner surface of the recess formed in the semiconductor substrate.

[0076] The second transfer robot 62 further transfers the substrate W to the electroless plating tank 20, where the electroless plating process is performed with a predetermined reducing agent and a predetermined plating liquid. With this process, as shown in FIGS. 7A and 7B, an electroless plating layer 41 is formed on the inner surface of a barrier layer 40. In this case, electrons generated at the solid-liquid interface due to decomposition of the

reducing agent are applied to the Cu^{2+} via the catalyst on the surface of the substrate, and hence Cu metal is deposited on the catalyst to form the copper layer 41. In addition to Pd, other transition metals such as Fe, Co, Ni, Cu, and Ag may be used as the catalyst.

[0077] Next, the substrate W is transferred to the electrolytic plating tank 22 by the transfer robot, and the copper layer 41 formed by the electroless plating process is connected to an electrode to perform the electrolytic plating process with a predetermined plating liquid, for thereby filling the recess 42 with electrolytic plating metal 43, as shown in FIGS. 7C and 7D.

[0078] After the electrolytic plating process is completed, the substrate is taken out by the second transfer robot and transferred to the rinse tank to be rinsed and then placed on a second temporary holding stage 67. The substrate is held by the first transfer robot 61 and transferred to the cleaning and drying device 60 to be cleaned and dried for finishing, and returned to the load/unload unit 14a, 14b. The substrate is finally transferred to a chemical mechanical polishing apparatus (CMP) to remove unnecessary plating metal from the surface of the substrate with the chemical mechanical polishing process.

[0079] FIG. 8 shows a plating apparatus according to another embodiment of the present invention. The plating apparatus comprises a vertical processing tank 24 as in the previous embodiment, and processing liquid circulating

devices 33a, 33b, 33c for circulating and supplying a respective processing liquid (electroless copper plating liquid, rinse water, and electrolytic copper plating liquid) to the processing tank 24. Supply of the processing liquid can be switched by switching valves 36a through 36c and 37a through 37c. The processing tank 24 comprises a processing container base 50 having an anode 54 and a shielding plate 55 therein, as in the example shown in FIG. 2, and can perform the electrolytic plating process.

10 | [0080] In this embodiment, for example, after the electroless plating process is completed, the plating liquid is returned to the reservoir tank 31a. A rinse water circulating pump 32b is operated to introduce rinse water into the processing tank 24, and then an electrolytic plating liquid is introduced from the reservoir tank 31c into the processing tank 24. After the electrolytic plating process is completed, a rinsing process is similarly performed. Thus, it is possible to eliminate such problems that plating liquids are mixed with each other. In this embodiment, the electroless copper plating process, the rinsing process, the electrolytic copper plating process, the rinsing process, and other processes can ~~continuously~~ be continuously performed in the same processing tank 24 without transferring a substrate, simply by changing processing liquids. Therefore, the present embodiment can decrease the number of the required tanks compared with the previous embodiment and can eliminate the need of a transfer robot for transferring a substrate between tanks, for

thereby compacting a installation frame. Further, throughput is increased as the transferring time can be eliminated.

[0081] FIG. 9 shows a plating apparatus according to still another embodiment of the present invention. A transferring rail 61a is extended from one side of a rectangular frame to the other side of the frame, and a transfer device (transfer robot) 61 is movably provided on the transferring rail 61a. A load/unload unit 41, a pre-treatment unit 68, an electroless plating unit 69, a first spin drying unit 70A, an electrolytic plating unit 71, and a second spin drying unit 70B are clockwise disposed in order so that these units surround the transfer robot 61. The pre-treatment unit 68 comprises an activator (SnCl_2 solution) tank or a catalysis (PdCl_2 solution) tank, for example.

[0082] FIG. 10 is a schematic view showing a configurational example of the electroless plating unit 69 shown in FIG. 9. The electroless plating unit 69 has a turntable 72 for holding a substrate W to be plated such as a semiconductor substrate thereon. A heater 73 for maintaining temperature is provided in the turntable 72, and the turntable 72 can ~~vertically~~ be moved vertically via a ball screw 85 by a motor 86 and rotated via a timing belt 83 by a motor 84.

[0083] A plating cell 92 having an opening in its lower surface is disposed above the turntable 72, and a seal packing 91 which is brought into close contact with the

plating substrate W held by a housing 96 is provided at the outer edge of the lower end of the plating cell 92. Specifically, when the turntable 72 is upwardly moved, a hermetically sealed space is formed in the plating cell 92 in such a state that the surface of the plating substrate W is brought into close contact with the seal packing 91. The hermetically sealed space has a volume sufficient for accommodating the minimum amount of plating liquid (electroless plating liquid) required for performing a predetermined plating on the surface of the plating substrate W, as described later.

[0084] A preparation bath 74 is disposed in the vicinity of the upper portion of the plating cell 92 and supplied with plating liquids A, B, C, and pure water D. An impeller 76a connected to an agitator 76 is disposed in the preparation bath 74, and a heater 81 is disposed in the preparation bath 74. A plating liquid in the preparation bath 74 is supplied to the plating cell 72 via a plating liquid supply valve 79.

[0085] A hot bath 75 is disposed in the vicinity of the outer portion of the preparation bath 74 so as to surround the preparation bath 74. An impeller 77a connected to an agitator 77 is disposed in the hot bath 75, and a heater 82 is disposed in the hot bath 75. The reference numeral 80 denotes a plating liquid discharge valve for discharging a plating liquid after the plating process is completed in the plating cell 92. A plating liquid discharged through the plating liquid discharge valve 80 flows into a waste liquid

tank 93. The reference numeral 78 denotes a pressure supply valve for supplying pressure into the plating cell ~~78~~ 92. The pressure in the plating cell 92 can be pulsed via the pressure supply valve 78 by a pressure pulsation generator
5 94.

[0086] The pressure pulsation generator 94 comprises a pressure regulator valve 87 for high pressure, a pressure regulator valve 88 for low pressure, a switching valve 89 for switching pressure, and a pneumatic pressure source 90, and can generate pressure pulsations having an amplitude of
10 0 to 1 MPa and a frequency of 0 to 10 Hz. The reference numerals P1, P2 denote pressure gauges.

[0087] In the electroless plating apparatus thus constructed, when a substrate W is plated, the plating
15 substrate W is held in a predetermined position on the upper surface of the turntable 72 positioned below the plating cell 92. In this state, the turntable 72 is moved upwardly via the ball screw 85 by the motor 86 to thus bring the upper surface of the plating substrate W into close contact
20 with the seal packing 91, ~~for~~ thereby closing the lower opening of the plating cell 92 to form a hermetically sealed space therein. At this time, the supply valve 79 is opened to supply the plating liquid Q in the preparation bath 74 to the plating cell 92.

[0088] The interior of the plating cell 92 has a volume
25 sufficient for accommodating the minimum amount of plating liquid Q required for performing a predetermined plating on the surface of the plating substrate W, and this minimum

required amount of plating liquid Q is accommodated in the interior of the plating cell 92. Here, the minimum required amount of electroless plating liquid is set within a range of amount of liquid that includes ions of solutes 1.5 to 20 times as many as a predetermined deposited metal equivalent. In the plating process, the pressure pulsation generator 94 applies a pressure pulsation to the plating cell 92 via the pressure supply valve ~~8~~ 78 at a predetermined amplitude and a predetermined frequency.

10 | [0089] As shown in FIGS. 11A through 11C, since the plating substrate W is held on the upper surface of the turntable 72 in such a state that the surface to be plated faces upwardly, hydrogen gas bubbles 98 certainly generated in the plating liquid Q in the electroless plating process
15 | ~~is~~ are moved upwardly due to buoyancy. Therefore, the number and the amount of bubbles remaining on the plating surface 97 of the plating substrate W and in fine grooves and holes are reduced, for thereby reducing the plating defects. Further, the minimum required amount of plating
20 | liquid Q is supplied to the hermetically sealed space in the plating cell 92, and the substrate is plated in a stationary state. Hence, the hydrogen gas bubbles 98 are not moved on the plating surface ~~87~~ 97, ~~for~~ thereby minimizing the amount of unevenly plated portions generated on the plating
25 | surface.

| [0090] The pressure of the hermetically sealed space in the plating cell 92 is set to be higher than atmospheric pressure and pulsed by the pressure pulsation generator 94.

Hence, as described above, the hydrogen gas bubbles 98 can be encouraged to dissolve into the electroless plating liquid Q by pressurization and simultaneously encouraged to separate from the plating surface 97 by pressure pulsation, as shown in FIGS. 11A through 11C.

[0091] The preparation bath 74 is disposed in the vicinity of the upper portion of the plating cell 92, and the minimum required amount of plating liquid prepared in the preparation bath 74 is supplied to the plating cell 92 just before the substrate W is plated. Hence, the plating process is completed before the occurrence of problematic reactions specific to the electroless copper plating, such as a Cannizzaro reaction or a disproportionation, which cause deterioration of the plating liquid and changes in concentration of the plating liquid composition after the preparation. Therefore, the plating process can be performed with a highly stable quality.

[0092] The plating liquid Q used for plating is discharged from the plating cell 92 via the plating discharge valve 80 into the waste liquid tank 93, where the plating liquid Q is processed as a waste liquid. Hence, the plating process can be performed with a highly stable quality. In addition, since the amount of plating liquid used per deposition is maintained to be the minimum required amount, it is possible to avoid increases in cost with the waste liquid and an excessive burden on the environment. Further, since the hot bath 75 is disposed above the plating cell 92 and the heater 73 for maintaining temperature is

disposed below the turntable 72, it is possible to maintain a fixed plating temperature, which is one of the most important factors governing the quality (uniformity of layer thickness, reproducibility, electric conductivity of the plating layer, etc.) of electroless plating.

5 **[0093]** After the plating process is completed, as described above, the plating liquid discharge valve 80 is opened to discharge the plating liquid in the plating cell 92 to the waste liquid tank 93. The turntable is moved
10 downwardly via the ball screw 85 by the motor 86, and a cleaning liquid (mainly pure water) is ejected from a cleaning nozzle 95 shown in FIG. 12 to the plating surface of the plating substrate W to clean the plating surface. In
15 this cleaning process, ~~the~~ a cleaning nozzle 95 is swung, and the plating substrate W is slowly rotated via the timing belt 83 by the motor ~~83~~ 84. After the cleaning process is completed, the plating substrate W is rotated at a high speed to spin off the cleaning liquid attached to the plating substrate W by centrifugal force.

20 **[0094]** After a seed layer is formed on the barrier layer in the wiring grooves by the electroless plating process, the substrate W is transferred to the first spin drying unit 70A by the transfer robot 61 and completely dried therein. Then, the substrate W is transferred to the electrolytic
25 plating unit 71, where the electrolytic plating process is performed. The electrolytic plating process will be described below with reference to FIGS. 13 and 14.

[0095] As shown in FIG. 13, the electrolytic plating

unit 71 comprises a plating tank 110, and the plating tank 110 comprises a plating tank body 111 and a substrate holding member 112 for holding a plating substrate W such as a semiconductor substrate in the plating tank body 111. The
5 substrate holding member 112 has a substrate holding portion 112-1 and a shaft portion 112-2, and the shaft portion 112-2 is rotatably supported in an inner wall of a cylindrical guide member 114 via bearings 115, 115. The guide member 114 and the substrate holding member 112 are vertically
10 movable at a predetermined stroke by a cylinder 116 provided on the top of the plating tank body 111.

[0096] The substrate holding member 112 is rotated in a direction indicated by the arrow A via the shaft portion 112-2 by a motor 118 provided on the inner side of the upper
15 portion of the guide member 114. A space C is formed in the substrate holding member 112, and a substrate presser member 117 having a substrate presser portion 117-1 and a shaft portion 117-2 is accommodated in the space C. The substrate presser member 117 is vertically movable at a predetermined
20 stroke by a cylinder 119 provided on the top of the shaft portion 112-2 in the substrate holding member 112.

[0097] An opening 112-1a communicating with the space C is formed below the substrate holding portion 112-1 of the substrate holding member 112, and, as shown in FIG. 14, a
25 step portion 112-1b on which the peripheral portion of the plating substrate W is placed is formed at the upper portion of the opening 112-1a. The peripheral portion of the plating substrate W is placed on the step portion 112-1b,

and the upper surface of the plating substrate W is pressed by the substrate presser portion 117-1 of the substrate presser member 117, for thereby clamping the peripheral portion of the plating substrate W between the substrate
5 presser portion 117-1 and the step portion 112-1b. The lower surface (plating surface) of the plating substrate W is exposed to the opening 112-1a. FIG. 14 is an enlarged view of the area B indicated in FIG. 13.

[0098] A flat plating liquid chamber 120 is provided
10 below the substrate holding portion 112-1 of the plating tank body 111, i.e., below the plating surface of the plating substrate W exposed to the opening 112-1a, and a flat plating liquid introduction chamber 122 is provided below the plating liquid chamber 120 via a perforated plate
15 121 having a large number of holes 121a. The recovery gutter 123 for recovering a plating liquid Q overflowing the plating liquid chamber 120 is provided outside of the plating liquid chamber 120.

[0099] The plating liquid Q recovered in the recovery
20 gutter 123 is returned to a plating liquid tank 124. The plating liquid Q in the plating liquid tank 124 is horizontally introduced to the plating liquid chamber 120 from both sides thereof by a pump 125. The plating liquid Q introduced to the plating liquid chamber 120 from both sides
25 thereof flows vertically into the plating liquid chamber 120 through the holes 121a formed in the perforated plate 121. A distance between the perforated plate 121 and the plating substrate W is set to be 5 to 15 mm. The flow of the

plating liquid Q passed through the holes 121a formed in the perforated plate 121 is brought into contact with the plating surface of the plating substrate W in such a state that the plating liquid Q flows upwardly as a uniform flow.

5 The plating liquid Q overflowing the plating liquid chamber 120 is recovered in the recovery gutter 123 and flows into the plating liquid tank 124. Specifically, the plating liquid Q is circulated between the plating liquid chamber 120 in the plating tank body 111 and the plating liquid tank
10 124.

[0100] The plating liquid level L_Q in the plating liquid chamber 120 is higher than the plating surface level L_W of the plating substrate W by a slight distance ΔL , and the plating liquid Q is brought into contact with the
15 whole surface of the plating substrate W.

[0101] An electrical contact 127 for electrically connecting with a connecting portion of the plating substrate W is provided in the step portion 112-1b of the substrate holding portion 112-1 in the substrate holding
20 member 112. The electrical contact 127 is connected to a cathode of an external plating power supply (not shown) via a brush 126. An anode 128 is provided on the bottom of the plating liquid introduction chamber 122 in the plating tank body 111, in confrontation with the plating substrate W.
25 The anode 128 is connected to an anode of the plating power supply. A transfer slit 129 for inserting and removing the plating substrate W with a substrate transfer jig such as a robot arm is formed at a predetermined position in the wall

of the plating tank body 111.

[0102] When the plating process is performed in the electrolytic plating unit thus constructed, the substrate holding member 112 is moved upwardly to a predetermined position (a position at which the plating substrate W held by substrate holding portion 112-1 opposes the transfer slit 129) together with the guide member 114 by actuating the cylinder 116, and simultaneously the substrate presser member 117 is moved upwardly to a predetermined position (a position at which the substrate presser portion 117-1 reaches the upper portion of the transfer slit 129) by actuating the cylinder 119. In this state, the plating substrate W is transferred to the space e_C in the substrate holding member 112 by the substrate transfer jig such as a robot arm and placed on the step portion 112-1b in such a state that the plating surface of the plating substrate W faces downwardly. At this state, the substrate presser portion 117-1 is moved downwardly to a position at which the lower surface of the substrate presser portion 117-1 is brought into contact with the upper surface of the plating substrate W, by actuating the cylinder 119, and hence the peripheral portion of the plating substrate W is clamped between the substrate presser portion 117-1 and the step portion 112-1b.

[0103] In this state, the substrate holding member 112 is moved downwardly to a position at which the plating surface of the plating substrate W is brought into contact with the plating liquid Q in the plating liquid chamber 120

(a position ΔL lower than the plating liquid level L_0) together with the guide member 114 by actuating the cylinder 116. While the substrate holding member 112 is being moved downwardly, the substrate holding member 112 and the plating substrate W are rotated at a low speed by actuating the motor 118. The plating liquid chamber 120 is filled with the plating liquid Q, and the plating liquid passed through the holes 121a formed in the perforated plate flows vertically upwardly in the plating liquid chamber 120. In this state, when a predetermined voltage is applied between the anode 128 and the electric contact 127 by the plating power supply, a plating current flows from the anode 128 to the plating substrate W to form the plating layer on the plating surface of the plating substrate W.

15 | **[0104]** During the plating process, the substrate holding member 112 and the plating substrate W ~~is~~ are rotated at a low speed by actuating the motor 118. This rotation at a low speed is set such that the vertical flow of the plating liquid Q in the plating liquid chamber 120 is not interrupted, and a plating layer having a uniform thickness can be formed on the plating surface of the plating substrate W.

25 | **[0105]** When the plating process is completed, the substrate holding member 112 and the plating substrate W are moved upwardly by actuating the cylinder 116. When the lower surface of the substrate holding portion 112-1 is positioned above the plating liquid level L_0 , the motor 118 rotates the substrate holding member 112 and the plating

substrate W at a high speed to spin off the plating liquid attached on the plating surface of the plating substrate W and the lower surface of the substrate holding portion 112-1. After the plating liquid is spun off, the plating substrate W is moved upwardly to a position corresponding to the transfer slit 129. When the substrate presser portion 117-1 is moved upwardly by actuating the cylinder 119, the plating substrate W is released from the substrate presser portion 117-1 in such a state that the plating substrate W is placed on the step portion 112-1b of the substrate holding portion 112-1. In this state, the substrate transfer jig such as a robot arm is inserted from the transfer slit 129 into the space C in the substrate holding member 112 to pick up the plating substrate W and transfer it to the exterior.

[0106] With the electrolytic plating unit 71 thus constructed, a plating substrate W in which holes having a diameter of $0.15 \mu\text{m}$ and a depth of $1.2 \mu\text{m}$ were formed was plated by the electrolytic plating process to fill the holes with copper. A plating liquid Q having the following composition, a current density of 2 A/dm^2 , and a temperature of 25°C was used, and a plating time was set to 150 seconds. The holes were efficiently filled with copper.

Composition of Plating Liquid Q

25	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	225 g/l		
	H_2SO_4	55 g/l		
	Cl^-	60 mg/l		
	Sulfur	compound	(N,	N-

dimethyldithiocarbamylpropylsulfonic acid) 5 mg/l

Macromolecular compound (PEG6000) 0.1 g/l

Nitrogen compound (safranine compound, janus green B) 2 mg/l

5 | [0107] When a plating liquid having a high concentration of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is used, as described above, a hole having a diameter of $0.15 \mu\text{m}$ and a depth of $1.2 \mu\text{m}$ can efficiently be filled with copper by plating.

10 | [0108] FIG. 15 shows a processing tank 25 which can continuously ~~performs~~ perform an electroless plating process and an electrolytic plating process with the same processing liquid. The processing tank 25 can perform an electrolytic plating process as with the processing tank shown in FIG. 8. In this processing tank, the electroless plating process is
15 | performed, and then the electrolytic plating process is directly performed by energization of a low current of less than 0.2 A/dm^2 . In this case, an electroless plating liquid is used as a plating liquid, and TMAH is used in place of NaOH or KOH usually used as a pH regulator in the
20 | electroless plating process, in order to prevent the semiconductor substrate from being contaminated. TMAH is an organic alkali chemical including a methyl group. It is necessary to avoid using a reducing agent liable to be decomposed, such as formalin, which has commonly been used.

25 | [0109] Conventionally, in the through hole plating of the printed circuit board, throwing power has been improved by a high throwing power bath ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 10-80 g/l) having a low Cu concentration. However, when trenches and via

holes of a semiconductor substrate are plated, not only throwing power but also ~~levelling~~ leveling of plating is required in order to prevent the generation of voids.

Further, since the high throwing power bath is easily
5 influenced by the flow of a plating liquid, it is desirable to use a plating liquid having a mid to high increased concentration for reducing the possibility of flow effects.

[0110] Various things were examined under the above preconditions. As a result, conventionally used baths such
10 as a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ low concentration (15-80 g/l) bath (high throwing power bath) superior in throwing power, or a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ high concentration (150-220 g/l) bath (decorative bath) superior in ~~levelling~~ leveling of plating were found not to be appropriate. A $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mid concentration (100-
15 150 g/l) bath was found to be appropriate for a damascene plating process which combines an electroless plating process and an electrolytic plating process of a semiconductor substrate.

[0111] As described above, according to the present
20 invention, an initial plating layer (seed layer) is formed with an electroless plating process, and then the recess in the substrate is filled with electrolytic plating metal while the initial layer serves as the feeding layer. Accordingly, the recess having a barrier layer of a high
25 electrical resistance can efficiently be filled with a void-free wiring metal, without the sputtering process or the CVD process in a series of plating processes. Therefore, the present invention can provide a method and apparatus for

plating a substrate to form wiring by efficiently filling a fine recess formed in a semiconductor substrate with plating metal without a void or contamination.

5 **Industrial Applicability**

[0112] The present invention is suitable for a method and apparatus for plating a substrate to fill a wiring recess formed in a semiconductor substrate with wiring metal such as copper, copper alloy, or the like.